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FORMATION OF THE $\text{YBa}_2\text{Cu}_2\text{NbO}_y$ PHASE IN THIN FILMS (POSTPRINT)

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Energy/Power/Thermal Division**

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Formation of the $\text{YBa}_2\text{Cu}_2\text{NbO}_y$ phase in thin films

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We report the systematic substitution of Nb at the Cu1 site of $\text{YBa}_2\text{Cu}_3\text{O}_y$ in thin films to form a new phase of $\text{YBa}_2\text{Cu}_2\text{NbO}_8$. These films were deposited on $\text{SrTiO}_3(100)$ crystals using pulsed laser deposition and deposited at an optimal temperature of 850 °C. Films were characterized using x-ray diffraction (XRD), atomic force microscopy, x-ray photoelectron spectroscopy (XPS), micro-Raman spectroscopy, and transmission electron microscopy. XRD of these films indicate *c*-axis oriented $\text{YBa}_2\text{Cu}_2\text{NbO}_y$ formation. XPS and micro-Raman spectroscopy analysis suggests Cu exists in the +2 state.

I. INTRODUCTION

Our group has previously investigated alternate functional oxide materials as possible buffer layers on metallic substrates for the high-temperature superconducting (HTS) $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (YBCO) coated conductor applications. In this context, the growth of $\text{YBa}_2\text{Cu}_x\text{M}_y\text{O}_z$ (YBCMO, M = transition metals) phases is considered for thin films. The coated conductors can also potentially be used for both direct current (dc) and alternating current (ac) applications. However, the optimal architectural configurations for these two applications can differ. In the ac-tolerant configuration, the buffer layer is ideally nonconducting to avoid eddy current and coupling losses, whereas in dc applications, a conducting buffer may be desirable for use of the substrate as a stabilization layer.^{1,2} Identifying a metal-to-insulating transition in the oxide buffer by means of chemical doping can serve as a dual-use buffer.

Previous investigations have studied the effects of the partial substitution of copper in the YBCO compound as $\text{YBa}_2\text{Cu}_{3-x}\text{M}_x\text{O}_{7-z}$ and have demonstrated that such substitutions degrade the superconducting properties of the material.³⁻⁷ Preferential occupancy cations in the two nonequivalent copper sites have shown to substantially affect superconductivity in the YBCO thin films, significantly depressing T_c for a 0.2 molar substitution.³⁻⁵ For the use considered here, complete suppression is necessary with additional doping while maintaining the appropriate epitaxial properties for subsequent YBCO growth.

The particular substitution of Nb can potentially produce a metal-to-insulating transformation in the electrical and structural properties. It has been reported by several researchers that a new structure of dielectric

buffer layers consisting of both insulator grains and superconducting grains can be produced by Nb doping at the copper sites in the YBCO structure.^{6,7} Srinivas et al.⁸ have reported Nb doping at copper site in thin films deposited on $\text{SrTiO}_3(100)$ substrates and the addition of V_2O_5 and Nb_2O_5 into YBCO thin films. Additionally, recent initial results have demonstrated the potential use of $\text{YBa}_2\text{Cu}_{3-x}\text{Nb}_x\text{O}_y$ (YBCN_xO) as a single buffer with a good lattice match, thermal expansion match, and chemical compatibility.^{7,9} However, successful implementation of YBCN_xO as a single buffer from a conducting to an insulating state depends on the electrical transition and epitaxial change to the $\text{YBa}_2\text{NbCu}_2\text{O}_8$ (YBCNO) doping level and whether this structure exists as a single phase. Even if YBCNO is superconducting, its properties may prove of benefit for other uses as a superconductor. Consideration of the relative substitutional occupancies of the Cu1 (chain) and Cu2 (plane) sites is key to determining such primary features as the oxygen site occupancy, the substitutional solubility, and the degree of degradation of the attendant superconducting properties.

Experimental evidence of Nb substitution at the Cu site for the $\text{LBa}_2\text{Cu}_3\text{O}_y$ cuprate (L = Y, lanthanide series) is dependent on the choice of L. Previously, Greaves and Slater¹⁰ reported the formation of the $(\text{La},\text{Pr})\text{Ba}_2\text{NbCu}_2\text{O}_8$ (LBCNO or PBCNO) tetragonal phase in bulk, but mentioned the $\text{YBa}_2\text{NbCu}_2\text{O}_8$ (YBCNO) phase does not form in bulk. Bremer and Langbein¹¹ also confirmed that the YBCNO phase does not exist in bulk. The reasons for not forming the YBCNO phase in the case of bulk compounds were discussed by researchers.^{10,11} Nb doping at the copper sites in $\text{YBa}_2\text{Cu}_3\text{O}_{7-z}$ (YBCO) to form $\text{YBa}_2\text{Nb}_x\text{Cu}_{3-x}\text{O}_{7-z}$ phases has been reported by these authors. More recently, Sathiraju et al.^{12,13} have reported Nb doping at copper sites in YBCO thin films

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deposited on $\text{SrTiO}_3(100)$ and have reported the growth of the YBCO phase along with YBCO films.

Lack of successful reports on single-phase formation of the YBCNO compound, although discouraging, does not mean that successful formation in thin films is impossible. Previous attempts to form this phase, among others, have used complex carboxylate solutions and stoichiometric mixtures of the intimately ground powders that were subsequently processed. Because of epitaxial growth on a crystalline substrate, thin film growth offers a potential mechanism to significantly stabilize growth of the YBCNO phase. Our results show the substitution of Nb at the Cu1 site in thin films. In this work, we report this substitution in YBCO films, creating the YBCNO phase in the thin film form.

II. EXPERIMENTAL

Stoichiometric $\text{YBa}_2\text{Cu}_2\text{NbO}_y$ (YBCNO) powder was prepared using Y_2O_3 , BaCO_3 , Nb_2O_5 , and CuO powders of 99.99% purity. Calcinations of the as-pressed pellets of mixed powder were carried out between 950–1250 °C temperatures. After the first calcinations, the pellets were reground and pressed into the desired target size, which was then sintered in air. The pulsed laser deposition (PLD) targets were formed using a hydraulic press, creating a diameter of 2.54 cm and a 4 mm thickness. The final density of the fabricated targets was ~70–80%. Using PLD, YBCNO films were deposited on SrTiO_3 T100Y substrates of the dimensions of 10 mm × 3 mm × 0.5 mm. A Lambda Physik LPX 305i excimer laser (Ft. Lauderdale, FL) was used at the KrF transition, 248 nm, with a 25 ns pulse. The target to substrate distance was kept constant at 6 cm with a laser beam spot size of 7 mm × 1 mm and 2.5 J/cm² laser energy. A laser frequency of 10 Hz was used. The deposition chamber was maintained at 250 m Torr oxygen partial pressure. A substrate temperature of 850 °C produced the optimal films. The typical thickness of the films studied ranged between 100–300 nm.

As-deposited YBCNO films were initially characterized using a Rigaku model x-ray diffractometer (XRD, The Woodlands, TX) and a micro-Raman spectrometer. Renishaw inVia Raman microscopy (Gloucestershire, UK) was used to study the Raman shifts at room temperature. Binding energy peak information was obtained with a Kratos AXIS Ultra x-ray photoelectron spectrometer (XPS; Manchester, UK). A monochromatic Al K_{α} x-ray line was used for enhanced spectral resolution. The analysis spot size was ~110 μm. Transmission electron microscopy (TEM) analysis was carried out in a Philips CM 200 TEM at 200 kV. Samples for TEM were prepared using a focused ion beam (FIB (Eindhoven, The Netherlands)) microscope. For TEM examination, a thin Pt protective layer was deposited on the top of YBCNO

film by dc sputtering. A 200 nm × 200 nm area film was selected and cut with a Ga ion beam (30 kV) and lifted out onto a Cu grid bar. Further thinning was done with a fine Ga beam (30 kV). The composition of the film was analyzed using energy dispersive x-ray (EDX) analysis.

Transport current measurements of the samples that were checked had current and voltage contacts patterned onto the films by dc magnetron sputtering deposition of Ag with 93 μm thickness. Transport current measurements were made in liquid nitrogen with the 4-probe method using pogo pins for current contacts. To check for a superconducting critical transition temperature (T_c) in the samples, an ac susceptibility technique was used with the amplitude of the magnetic sensing field varied from 0.025 to 2.2 Oe at a frequency of 4 kHz. Those samples measured by ac susceptibility had no Ag contacts deposited on them. Samples were mounted onto the end of a sapphire rod and measured as the samples were slowly warmed.

III. RESULTS AND DISCUSSION

Electrical resistivity measurements of the YBCNO films indicate no superconducting transition down to 77 K. However, blockages may be present and/or the T_c may be below 77 K. The ac susceptibility measurements were also performed on the samples, which indicated no transition, even down to 4 K. This indicates an effective loss of superconductivity for YBCNO. The loss of T_c values cannot be attributed simply to the depletion of oxygen since films were subsequently oxygenated, and oxygen content is observed to correctly increase relative to YBCO to maintain the proper charge balance in this new compound.

Figure 1 shows the x-ray pattern of a highly-oriented YBCNO film deposited on strontium titanate (STO) at 850 °C. A PBCNO (P = Praseodymium) (GPDF file no. 45-0580) standard x-ray pattern was used for sample identification since Pr ionic radii and Y ionic radii are comparable. On the basis of this analysis, the YBCNO phase appears to be tetragonal. However, it is difficult to conclude the structure of YBCNO solely from this XRD data. There are no significant differences in the peak

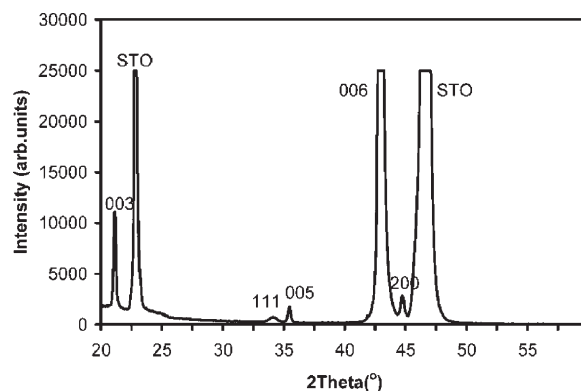


FIG. 1. 2θ XRD scan of an $\text{YBa}_2\text{Cu}_2\text{NbO}_8$ thin film.

positions and peak intensities for either the YBa_2NbO_6 (YBNO) or the YBCNO compounds in XRD patterns. While discussing the solid solutions of $\text{YBa}_2\text{Cu}_{3-x}\text{Nb}_x\text{O}_y$ compounds in bulk form, Bremer and Langbein reported the formation of YBNO and CuO,¹¹ concluding that the hypothetical compound $\text{YBa}_2\text{Cu}_2\text{NbO}_8$ is less stable than a mixture of the complex perovskite compound and an appropriate quantity of CuO. In this case, the peaks of both the YBNO and CuO phases should show up in the XRD in the case of our thin films, too. However, no such distribution of peaks is present, for example, a combination of YBNO and CuO phases or other possible phases such as YNbO_4 or $\text{Ba}_2\text{NbCuO}_{5.5}$, although some minor misorientations appear.

Micro-Raman spectra obtained at room temperature are shown in Fig. 2. Raman shifts were observed at 295, 346, 383, 633, and 819 cm^{-1} wave numbers. In comparing these spectra with the Raman spectra of an YBCO film, the main YBCO orthorhombic Raman mode at 321 cm^{-1} was shifted to 340 cm^{-1} . This shift, as well as the absence of the other YBCO orthorhombic Raman mode at 500 cm^{-1} in the YBCNO film, may indicate there is a phase transformation from orthorhombic to tetragonal. However, since the Raman modes of YBCNO

can be different from YBCO, the Raman studies are not conclusive in and of themselves, but provide additional evidence of an alternate phase formation.

The Cu(2p) binding energy of the film is shown in Fig. 3(a). While studying the oxidation behavior of Cu on Si substrates, Gao et al.¹⁴ demonstrated a consistent behavior of CuO with XPS and XRD. If Cu(2p) is present in the CuO form, it should show 4 peaks at different binding energies, but no such structure is seen in the YBCNO films. It is further evident from Fig. 3(b) that there is no CuO segregation in our films, indicating that Cu exists in compound form with the other elements. This offers additional evidence that a new distinct phase is formed in our films. Data from the O(1s) binding energy of YBCO and YBCNO films suggests that oxygen in YBCNO and YBCO has the same kind of binding energy. This is also indicative that oxygen is in a single compound form and not in multiple compounds.

Figure 4 shows the cross section of YBCNO film deposited on a STO substrate. The film thickness is ~ 175 nm with the STO substrate at the bottom of the figure. The top layer is a Pt protective layer. In the

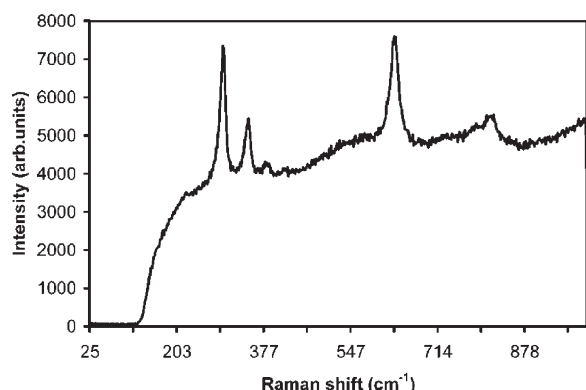


FIG. 2. Micro-Raman spectra of YBCNO obtained at room temperature.

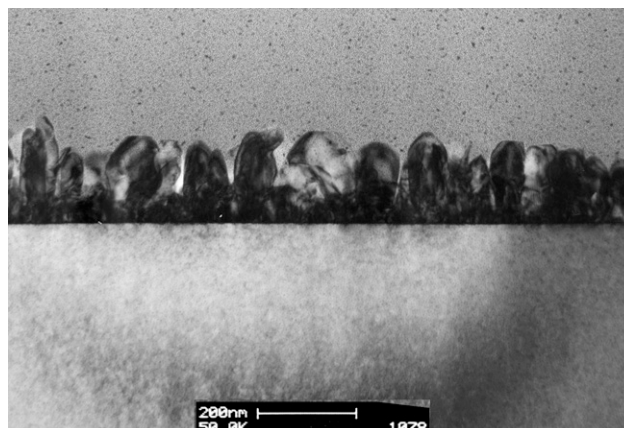


FIG. 4. Cross-sectional TEM image of the as-grown YBCNO film.

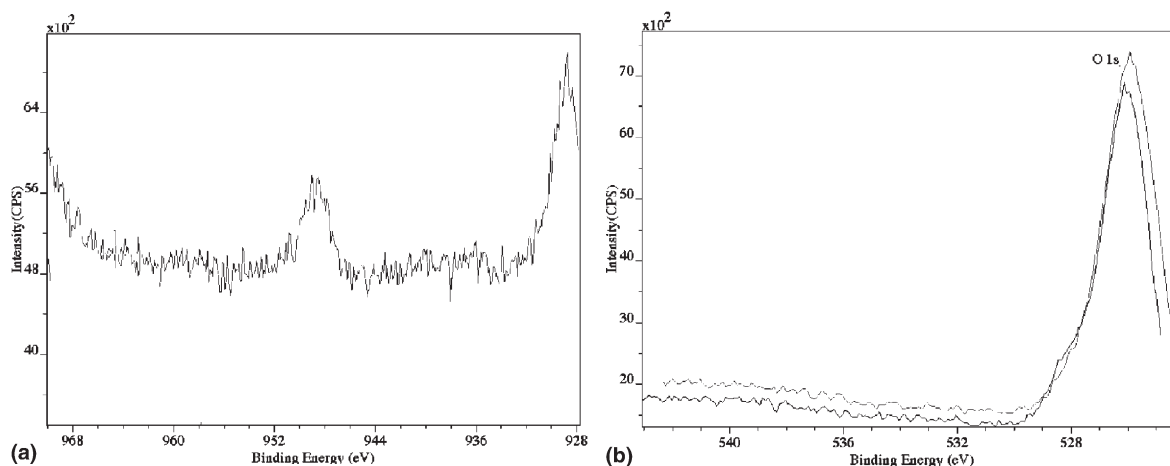


FIG. 3. XPS spectra: (a) Cu(2p) peak for YBCNO and (b) O(1s) peak for both YBCNO and YBCO.

middle, both columnar and highly refined grains, which make up the YBCNO film, are visible. The initial layers of the material are likely under strain, which gets progressively relaxed as the film thickness increases.

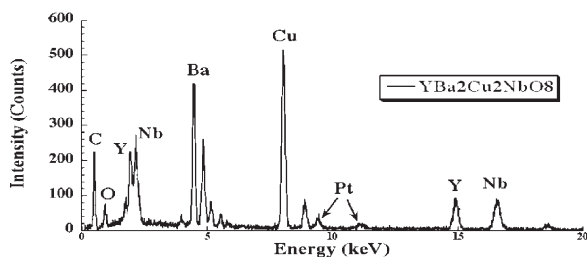


FIG. 5. TEM EDX spectrum recorded from one of the columnar grains imaged in Fig. 4.

The fine grains occur at the film/substrate boundary. Figure 5 shows a TEM EDX spectrum recorded from one of the columnar grains. In this figure, the Y and Nb Ka peaks have an intensity ratio of very nearly one. The preparation technique employs a Cu grid onto which the thin foil is attached. This leads to an artificially elevated level of Cu in the EDX spectrum. When this excess Cu intensity is taken into account, the Ba L peak and Cu K peak intensity ratio is close to unity and indicates a ratio of Ba or Cu with Y of 2:1. These observations then suggest a compositional stoichiometry of $\sim\text{YBa}_2\text{Cu}_2\text{NbO}_x$.

A selected-area diffraction pattern from the YBCNO film superimposed with the STO substrate is shown in Fig. 6. The pattern in Fig. 6(a) is oriented along the

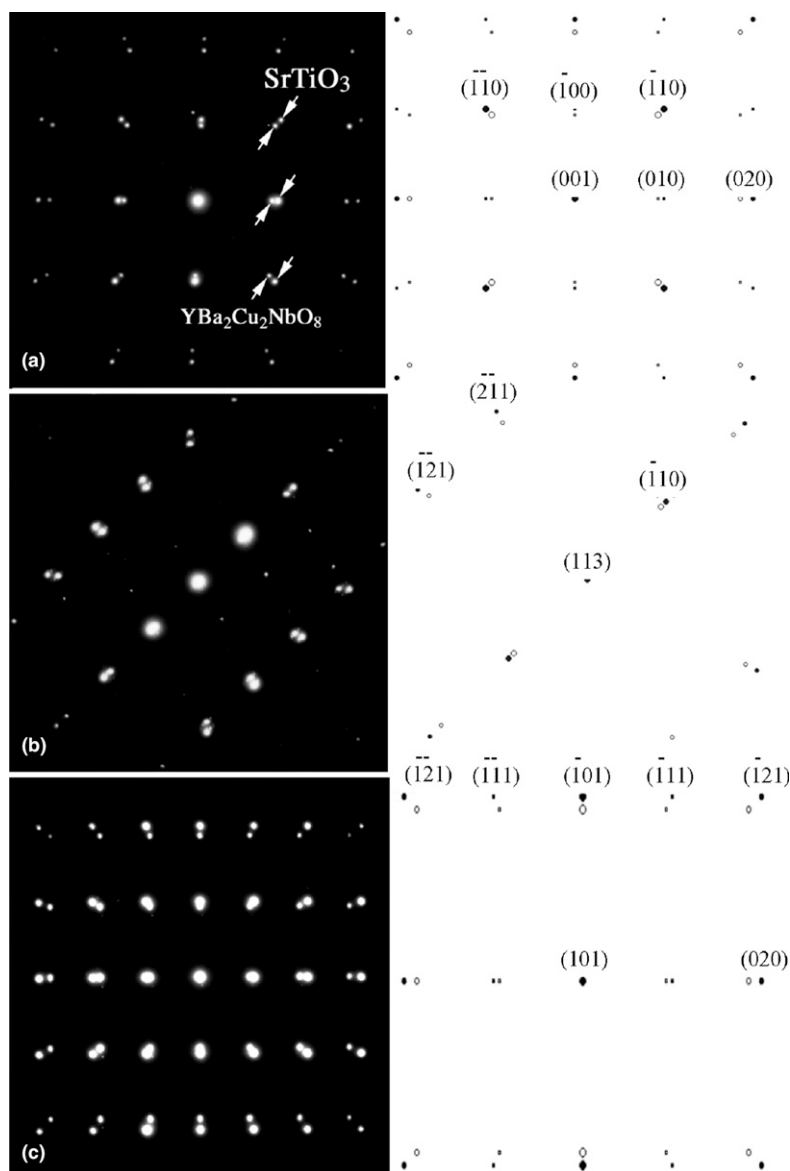


FIG. 6. Selected-area diffraction patterns of the YBCNO film on a STO substrate: (a) 001 orientation of SrTiO_3 and comparison with YBCNO phase, (b) 103 orientation of STO and comparison with YBCNO, and (c) 101 orientation of STO substrate and comparison with YBCNO phase.

[001] axis of the cubic SrTiO_3 substrate and contains strong {200} and {110} type reflections. Weak {100} type reflections are also visible here and confirm the lattice parameter of $\sim a_o = 0.391$ nm (STO). The STO phase was used to calibrate the lattice parameter of the new phase, which has $a_o \sim 0.40$ nm. While this electron diffraction pattern suggests that the $\text{YBa}_2\text{Cu}_2\text{NbO}_x$ phase has one fourfold axis of symmetry, it is unclear whether the structure is cubic (as the substrate) or tetragonal. Our selected-area diffraction analysis suggests that it is cubic. The presence of Nb at the Cu1 site may result in an increase in z (O4) relative to that observed in YBCO since $\text{M}^{5+}\text{--O}$ bonds are longer than Cu–O distances. This gives rise to longer Cu2–O2 bond distances relative to those in YBCO. From XRD data its lattice parameters are determined, $a \sim 0.4$ nm.

IV. SUMMARY

The YBCNO phase formation is indeed possible with respect to charge balance. Because of the Nb substitution at the Cu1 site, there is an increase in positive charge, which should be compensated with a negative charge of oxygen or by a decrease in Cu valence. Complete charge balance is expected in the case of $\text{YBa}_2\text{Cu}_2\text{NbO}_8$. If Nb substitutes at Cu1 sites in the basal plane, it may introduce extra oxygen at the vacant O5 sites. Because the structure cannot stabilize in bulk form, single crystal substrates whose lattice parameter matches with YBCNO can act as a template aiding the formation of $\text{YBa}_2\text{Cu}_2\text{NbO}_8$. This has been demonstrated in this work using PLD at substrate temperatures of 850 °C and above.

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